EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH
CERN – EST

STUDY OF THE RESIDUAL SURFACE RESISTANCE OF NIOBIUM FILMS AT 1.5 GHZ

C. Benvenuti, S. Calatroni, P. Darriulat, M.A. Peck, A. M. Valente and C.A. Van't Hof

Abstract

Potential contributions to the residual surface resistance of niobium films exposed to 1.5 GHz microwaves are reviewed and studied. These include the oxidation of the film surface, the formation of hydride precipitates, the contamination by noble gas atoms and the presence of macroscopic film defects such as those resulting from the roughness of the substrate. Particular attention is given to the dependence of the residual resistance on the amplitude of the microwave. Results similar to those obtained for bulk niobium provide strong evidence against the conjecture that the small size of the film grains should be a fundamental limitation to the production of films having a low residual resistance.

1. INTRODUCTION

The presence in small concentrations of non-magnetic impurities and defects having dimensions smaller than the coherence length only slightly deteriorates the superconducting properties of a metal [1]. The main consequence is a decrease of the critical temperature T_c and of the energy gap Δ, with no visible effect at zero temperature, nor, in practice, at temperatures T much smaller than T_c. In particular no residual resistance is generated which would add to the surface resistance of a superconductor exposed to microwaves, but only the BCS resistance [2-4] is slightly modified.

However, when the dimensions of such impurities and defects are well in excess of the coherence length, the overall coherence of the superconducting state is no longer preserved and the Anderson theorem [1] no longer applies. To the extent that such impurities and defects are visible to the incident microwave, they may cause additional losses which persist at zero temperature. Depending on their geometry and location (in particular a microwave will sense the surface of a superconductor over only a few penetration depths) and on the density of free electrons which they contain (normal conductors and insulators are expected to behave differently) such impurities and defects may therefore generate a residual resistance term.

In the intermediate regime, when the dimensions of the impurity or defect are of the scale of the coherence length, Cooper pairs may tunnel across their boundaries and a Josephson junction is obtained [5]. This is the situation in "weak links" models used to describe the properties of granular high Tc superconductors [6]. In such models Josephson junctions are assumed to be present at grain boundaries and the resulting contribution to the surface resistance depends on the relative values of the junction critical current and of the surface current induced by the incident microwave.

The subject of the present work is the study of the residual resistance of niobium films exposed to 1.5 GHz microwaves. In a previous publication [7] arguments were presented against the conjecture [8-10] that most of the residual resistance of niobium films should be blamed on their small grain size (typically 100 to 200 nm compared to 100 μm or so in the bulk case). Such a conjecture, inspired from results obtained on granular high T_c superconductors [6], postulates the presence of "weak links" at grain boundaries and implies the existence of a fundamental limitation to the production of low residual resistance niobium films. The results presented here provide additional evidence against such a conjecture.

The study explores various mechanisms which are potential contributors to the generation of a non-zero residual resistance. These include the oxidation of the film surface, the presence in the film of a significant quantity of atoms of the noble gas used for sputtering, the possible existence of hydride precipitates and defects such as those resulting from the presence of impurities on the substrate (before the film was grown) or from the shadow effect occurring on a rough substrate when the sputtering incidence angle is large enough. A detailed description of the experimental method, including the production of films grown on the inner wall of copper cavities, the measurement of their superconducting properties (in particular of their surface resistance using 1.5 GHz microwaves) and their characterisation in terms of a limited number of variables is available in Reference [7]. It is not repeated here.

Particular attention is given to the study and understanding of the dependence of the residual resistance on the amplitude of the microwave. In practical applications this may be an important limitation to the performance at high fields. In most cases a linear dependence on the magnetic component H_{rf} of the microwave gives a fair description of the data as long as H_{rf} does not exceed some field emission threshold, H_{fe}, beyond which the residual resistance increases nearly exponentially [11-12]. This is illustrated in Figure 1 where typical data are shown together

with the result of a fit to the form $R_{res} = R_{res}{}^0 + R_{res}{}^1 H_{rf}$ restricted to an interval $H_{low} \leq H_{rf} \leq H_{fe}$ defined as the largest interval over which a good χ^2 can be obtained. Beyond H_{fe} an additional nearly exponential term is necessary to describe the effect of field emission, the occurrence of which is signalled by the emission of X-rays and by the presence of a small electron current collected on the output antenna [7]. As field emission is abundantly studied in the literature [12] and is usually nothing but the result of the presence inside the cavity of defects (foreign particles, small protrusions from the surface), the scope of the present work is restricted to the interval $0 \leq H_{rf} \leq H_{fe}$ where field emission does not occur. On the low side small deviations from the linear fit are occasionally observed, causing H_{low} to depart from zero. Their origin is not understood but in most cases they are small enough to be ignored.

2.   MACROSCOPIC FILM DEFECTS

The roughness of the substrate is known to increase the residual resistance of the films grown on the inner wall of radiofrequency cavities [13]. Films grown on hydroformed copper (roughness $\cong 1$ μm) have a larger residual resistance than films grown on spun copper (roughness $\cong 0.2$ μm) by $\Delta R_{res}{}^0 \cong 13$ nΩ and $\Delta R_{res}{}^1 \cong 1.2$ nΩ/mT on average. As sputtering takes place at an average angle of incidence $\theta_{sp} \cong 15°$, reaching up to $50°$ near the iris, irregularities of the substrate act as obstacles and produce film inhomogeneities in their shadow [14]. The deterioration of the film quality resulting from an increase of the incidence angle has been studied on samples produced for this purpose. Figure 2 shows the result of an analysis of SEM micrographs of samples produced at different incidence angles (the standard deviation of the grey levels of all pixels is used as a measure of the amount of irregularities). The conductance to helium gas of films separated from their substrate by chemical etching has been measured with an accuracy of $\cong 30\%$. The results show a significant increase of the film porosity with θ_{sp}. The fraction of the film surface permeable to helium gas increases from $\cong 4.4$ ppm at the equator ($\theta_{sp} \cong 9°$) to $\cong 25$ ppm at the iris ($\theta_{sp} \cong 50°$).

In addition to the intrinsic roughness of the substrate, accidental contributions due to dust particles or damage caused by defective polishing may play an important rôle. The standard method of chemical polishing described in Reference [7] is known to produce holes, typically 0.3 μm in diameter, the more so the longer it lasts. Figure 3a shows a micrograph of a chemically polished sample and illustrates clearly the presence of such holes.

A significant improvement was achieved by using instead electropolishing which produces much smoother surfaces (Figure 3b) resulting in lower residual resistances (Figure 4). The values obtained this way are comparable to those obtained with bulk niobium, in clear contradiction with models claiming that the small grain size of niobium films should fundamentally prevent the production of low residual resistance films because of the presence of "weak links" at grain boundaries [8-10]. Moreover the grains of films grown on oxide-free copper are known [15] to be larger than those of films grown on oxidised copper by an order of magnitude. But the residual resistances of both types of films are found to be similar, if anything those of films grown on oxide-free copper may be slightly larger [13]. This provides additional and spectacular evidence against the relevance of weak link models to the films under study.

3.   OXIDES, HYDRIDES AND NOBLE GASES

The presence of impurities in a film can be expected to be a source of residual resistance. Oxygen, hydrogen and noble gases deserve special attention. The former two have been studied extensively in the case of bulk niobium, the latter is specific to films grown by sputtering in a noble gas atmosphere.

In practical applications such as the manufacture of RF cavities, it would be technically difficult to prevent the formation of a thin oxide (Nb_2O_5) layer on the film surface. Fortunately, in the case of bulk niobium, such a layer is harmless and does not produce more than $\cong 1.5$ nΩ of residual resistance [16,17]. The cavities considered in the present study are vented to dry air after sputtering as soon as they have cooled down to room temperature. They are then rinsed using high-pressure water before being evacuated and studied. The thickness of the oxide layer has been measured by Auger electron spectroscopy depth profiling and found not to exceed 6 nm. There is no reason to suspect that it might be more harmful than in the bulk niobium case. Indeed the mere fact that values of R_{res}^{0} and R_{res}^{1} as low as $\cong 1$ nΩ and $\cong 0.2$ nΩ/mT respectively have been obtained without taking any particular precautions to reduce the formation of an oxide layer is sufficiently convincing evidence. As a further check on a possible influence of the niobium oxide layer, a cavity has been produced according to the standard procedure [7] except for a thin aluminium overlayer ($\cong 10$ nm) grown on top of the niobium film before exposing it to air, resulting in the subsequent formation of a thin protective alumina layer. No significant effect has been observed.

Hydrogen is known to be a potentially important cause of residual resistance for bulk niobium cavities [18-20]. It is understood to result from the formation of hydride precipitates having typical dimensions ranging between several hundred Å and a few μm, occurring in a range of temperatures between $\cong 70$ K and $\cong 170$ K. Such a formation can be prevented by rapid cool-down, crossing the range of dangerous temperatures fast enough to make sure that the dissolved hydrogen atoms have no time to nucleate in regions of sufficient concentration before their mobility is reduced to negligibly small values. It can also be prevented by using niobium of low residual resistivity ratio, in which case the hydrogen atoms, being trapped by defects and impurities on their way to regions of possible hydride formation, have no chance to cluster and are therefore made innocuous.

In order to study what happens in the case of niobium films a number of cavities prepared under various conditions were loaded with hydrogen and residual resistances as high as a few $\mu$$\Omega$ were occasionally measured [13]. A detailed account of these measurements will be published elsewhere. The measurement of the hydrogen concentration in films is performed by studying the temperature dependence of the hydrogen pressure p_{H_2} present in the cavity volume when the film has been loaded with a known quantity of hydrogen, care being taken to prevent oxidation between coating and loading. According to Sievert's law, $p_{H_2} \propto c_H^2 \, exp(-2\, E_{act}/kT)$, where E_{act} is the activation energy and c_H the hydrogen concentration in the film. Increasing c_H by known quantities it is then possible to measure simultaneously E_{act} and the hydrogen concentration in the unloaded film. Figure 5 displays two typical sets of data, up to 350 ºC. They show that the reversible equilibrium regime to which Sievert's law applies is only reached after a first heating cycle during which defects acting as trapping sites for hydrogen are annealed and, in the case of films grown on oxidised copper, the interfacial oxide layer is dissolved. While the total concentration of hydrogen is measured at 0.4 (*resp.* 1.1) $\pm$ 0.1 at. ‰ for films grown on oxidised (*resp.* oxide-free) copper, no clear evidence is obtained that all the hydrogen dissolved in the film has been freed, or if even higher temperatures are necessary to anneal all the trapping sites. A detailed understanding of the amount and relative roles played by possible trapping sites (dislocations, oxygen atoms from the dissolved interfacial oxyde layer, etc…) requires additional measurements well beyond the scope of the present work.

Comparative degassings of coated and uncoated cavities suggest that an important fraction of the hydrogen contained in the film comes from the outgassing induced in the coating system by the sputtering plasma and from hydrogen dissolved in the sputtering cathode, in particular for films grown in the double cathode sputtering apparatus. However, a small contribution of hydrogen dissolved in the copper substrate cannot be excluded. The exposure of the film surface to laboratory air prior to the RF measurement, even after a dry air oxidation, favours the

formation of hydrogen-containing surface oxides [21] which also increase the total hydrogen content of the film, albeit in a different trapping state. The understanding of the relative importance of all these potential sources of hydrogen also requires further study. Here, it should be sufficient to note that hydrogen has never been found to be a major contributor to the residual resistance of films prepared under standard conditions. However, the occasional measurement of very high residual resistances in the case of loaded films shows how important it is to keep the hydrogen concentration in the film below the per mil level.

Sputtered films are known to contain atoms of the noble gas used in the sputtering discharge. The issue was amply discussed in Reference [7] and the dependence of the noble gas concentration on its atomic mass and on the stresses present in the film (*i.e.* in practice on the nature of the substrate) has also been studied [15]. As further developed in Reference [22], the pinning properties of the film suggest that at least part of the trapped gas tends to cluster in the form of solid "bubbles". It is therefore natural to expect that the trapped noble gas atoms might contribute to the generation of a non-zero residual resistance term. However, one must keep in mind the small dimensions of typical solid bubbles, $\cong 3$ nm (*i.e.* one tenth of a coherence length) and the fact that they are not expected to contain free electrons. Indeed, as shown in Figure 6, the residual resistances of films grown using xenon, krypton and argon do not significantly differ. Only in the case of neon, or of neon rich (>70%) neon-argon mixtures, does the residual resistance increase significantly. However the large spread of data of a same type, typically ±50% in both R_{res}^{0} and R_{res}^{1}, prevents the detection of a small difference between two different types. Therefore, small differences between xenon, krypton and argon data cannot be excluded.

4.   DISCUSSION OF THE RESULTS

The main results of the present study are the production of niobium films having very low residual resistance over a wide range of microwave amplitudes and the identification of the smoothness of the substrate as the main factor for this achievement. Rather than weak links at grain boundaries, the main cause for the significantly larger residual resistances which were commonly obtained in the past is now identified as being the presence within the film of islands of non superconducting defects. Of course a contribution of grain boundary weak links at the level of a few nΩ for R_{res}^{0} and a few tenths of nΩ/mT for R_{res}^{1} cannot be excluded but above such a level the small grain size characteristic of sputtered films cannot be blamed for the occasional generation of important residual resistances. The new picture emerging from this study calls for some comments. Residual resistances (by definition at $T = 0$) are trivially expected not to depend on the microwave amplitude, both in the case of homogeneous superconductors and in the case of homogeneous normal conductors, inhomogeneities being a prerequisite for non linearity. Indeed the picture of weak links located at grain boundaries and the present picture of islands of non superconducting defects both explain the generation of important residual resistances by the presence of inhomogeneities, which in these cases only differ by their geometry. The results sketched in Section 3 on the effects of oxides, hydrides and noble gases are consistent with the present picture and, at the same time, point to the relevance of the average defect size (relative to the coherence length) and of the density of free electrons which the defects contain. A quantitative assessment of the validity of the suggested picture would require a microscopic description which goes well beyond the scope of the present work. Basically, such a microscopic description would imply an extension to microwaves of the McMillan picture of the proximity effect [23], very much as the authors of References [2,3] extended the BCS theory to microwaves. To our knowledge this has not been done yet. Qualitatively however, one might expect the proximity effect, which smears the superconductor-normal conductor boundary around a defect over a distance with a scale of the coherence length, to cause a linear increase with the amplitude of the microwave of the area of the region containing unpaired electrons. One might also expect the nature of the defect, essentially normal

conductor or insulator, to be crucial in defining both the density of free electrons in the defect and the boundary conditions of the Maxwell equations describing the system. One might then hope to obtain in this way a quantitative understanding of the linear dependence of the residual resistance on the amplitude of the microwave, *i.e.* a quantitative description of R_{res}^{1}. An additional and independent argument, which might give support to the picture suggested here, is its possible extension to the radiofrequency losses induced by the presence in the film of strongly pinned fluxons. There exist interesting similarities between the relative properties of R_{res}^{0} and R_{res}^{1} on one hand and of R_{fl}^{0} and R_{fl}^{1} on the other. This is commented in more detail in Reference [22].

An important consequence of the present work is its implications for the large scale production of radiofrequency cavities for particle accelerators. Today, this is by far the main industrial application of RF superconductivity and the present results provide ample evidence for preferring the film technology to the more conventional and more commonly accepted bulk technology. Arguments along this line are developed in Reference [24].

ACKNOWLEDGEMENTS

REFERENCES

[1]   P.W. Anderson, J. Phys. Chem. Solids 11(1959)26.

[2]   D.C. Mattis and J. Bardeen, Phys. Rev. 111 (1958) 412.

[3]   A.A. Abrikosov, L.P. Gor'kov and I.M. Khalatnikov, Zh. Eks. Teor. Fiz. 35(1958)265 and JETP 35(1959)182.

[4]   J.P. Turneaure, J. Halbritter and H.A. Schwettman, J. Supercond. 4(1991)341.

[5]   B.D. Josephson, Phys. Lett. 1(1962)251 and Adv. in Phys. 14(1965)419.

[6]   T.L. Hylton, A. Kapitulnik, M.R. Beasley, J.P. Carini, L. Drabeck and G. Gruener, Appl. Phys. Lett. 53(1988)1343.

[7]   C. Benvenuti, S. Calatroni, I.E. Campisi, P. Darriulat, M.A. Peck, R. Russo and A.-M. Valente, Physica C 316(1999)153.

[8]   B. Bonin and H.Safa, Supercond. Sci. Technol. 4(1991)257.

[9]   C. Attanasio, L. Maritato and R. Vaglio, Phys. Rev. B43 (1991) 6128 and IEEE Trans. Mag. 27(1991)1920.

[10] J. Halbritter, J. Supercond. 5(1992)331, 8(1995)691 and 10(1997)91.

[11] C. Benvenuti, S. Calatroni, P. Darriulat, M.A. Peck, A.-M. Valente and C.A. Van't Hof, "Fluxon induced resistance and field emission", CERN Internal Report EST/2000-004 (SM), submitted for publication in Physica C.

[12] D. Moffat, P. Barnes, T. Flynn, J. Graber, L. Hand, W. Hartung, T. Hays, J. Kirchgessner, J. Knobloch, R. Noer, H. Padamsee, D. Rubin and J. Sears, Part. Accel. 40(1992)85 and references therein.

[13] C. Benvenuti, S. Calatroni, I.E. Campisi, P. Darriulat, M.A. Peck, R. Russo and A.-M. Valente, IEEE Trans. Appl. Supercond. 9(1999)900.

[14] G.S. Bales and A. Zangwill, J. Vac. Sci. Technol. A9(1991)145.

[15] C. Benvenuti, S. Calatroni, P. Darriulat, M.A. Peck and A.-M. Valente, "Influence of the nature of the substrate on the growth of superconducting niobium films", CERN Internal Report EST/2000-005 (SM), submitted for publication in Thin Solid Films.

[16] F.L. Palmer, Ph. D. Dissertation, Cornell University, Ithaca, N.Y., USA, 1988 and references therein.

[17] J. Halbritter, Proc. 2nd Workshop on RF Supercond., H. Lengeler ed., CERN, Geneva, 1984, p.427.

[18] B. Bonin and R.W. Roeth, Proc. 5th Workshop on RF Supercond., D. Proch ed., DESY, Hamburg, Germany, 1991, DESY-M-92-01, p.210 and references therein.

[19] S. Isagawa, J. Appl. Phys. 51(1980)4460 and 6010.

[20] T. Schober, Scripta Metallurgica 7(1973)1119.

[21] A. Daccà, Ph. D. Dissertation, Genova University, Italy, 1999

[22] C. Benvenuti, S. Calatroni, P. Darriulat, M.A. Peck and A.-M. Valente, "Fluxon pinning in niobium films", CERN Internal Report EST/2000-003 (SM), submitted for publication in Physica C.

[23] W.L. McMillan, Phys. Rev. 175(1968)559.

[24] V. Arbet-Engels, C. Benvenuti, S. Calatroni, P. Darriulat, M.A. Peck, A.-M. Valente and C.A. Vant' Hof, "Superconducting niobium cavities, a case for the film technology", CERN Internal Report EST/2000-001 (SM), submitted for publication in Part. Accel.

Figure 1 - The dependence of the residual resistance of a typical film on H_{rf}. The line is the result of the linear fit used to define $R_{res}{}^0$ and $R_{res}{}^1$ as described in the text. Here $H_{low} = 1$ mT, $H_{fe} = 10$ mT, $R_{res}{}^0 = 11.4$ nΩ and $R_{res}{}^1 = 1.03$ nΩ/ mT.
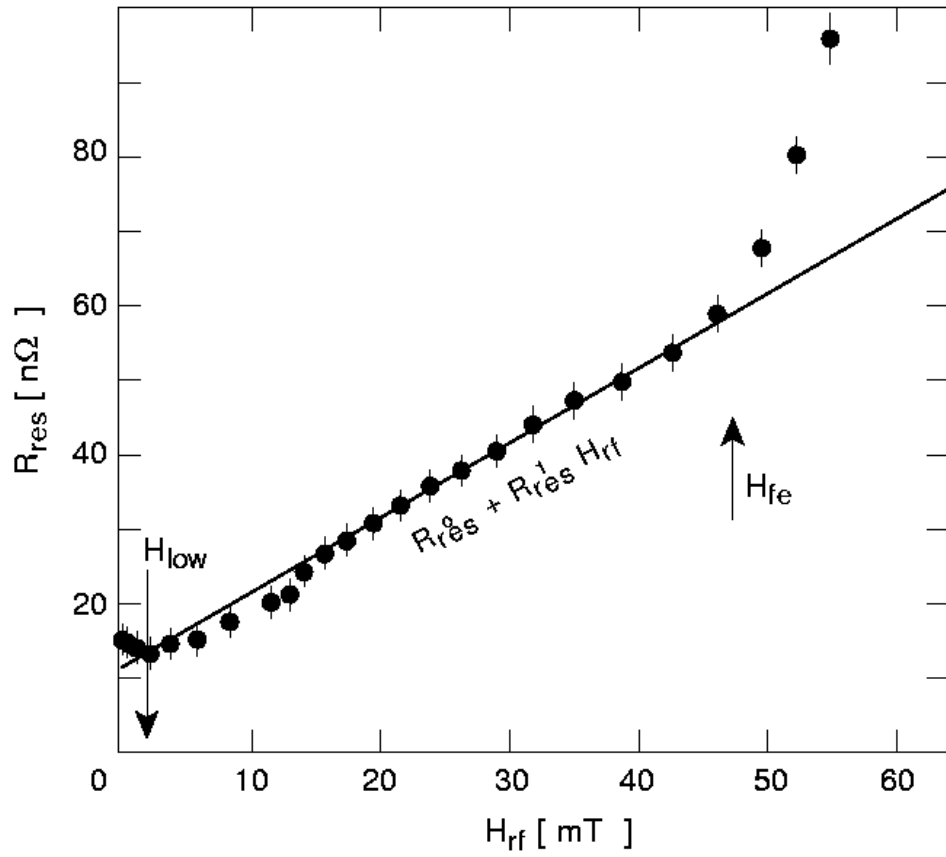
Figure 2 - Macroscopic film defects: the standard deviation of the grey levels of all pixels from SEM micrographs of films grown at different incidence angles.
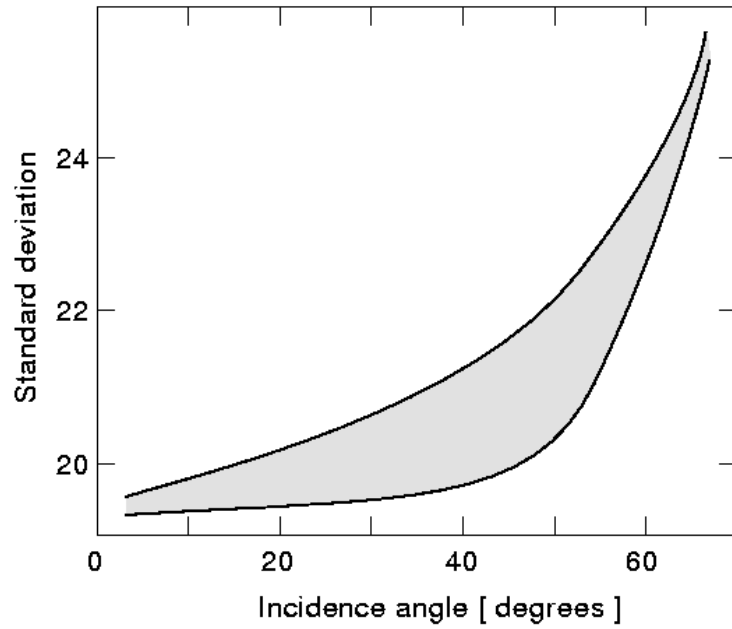
Figure 3 - Micrographs of chemically polished (a) and electropolished (b) copper substrates.
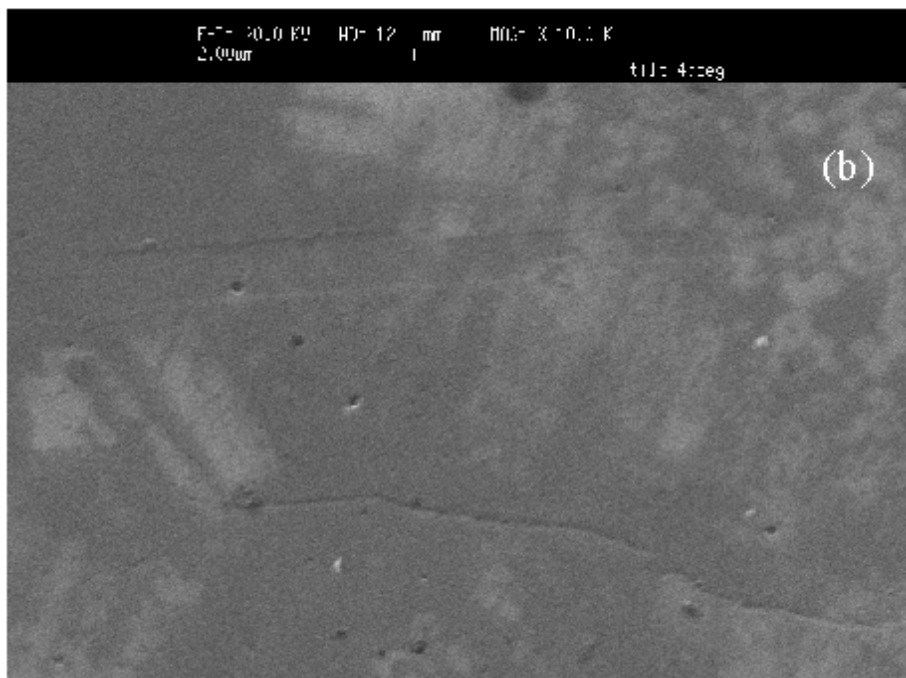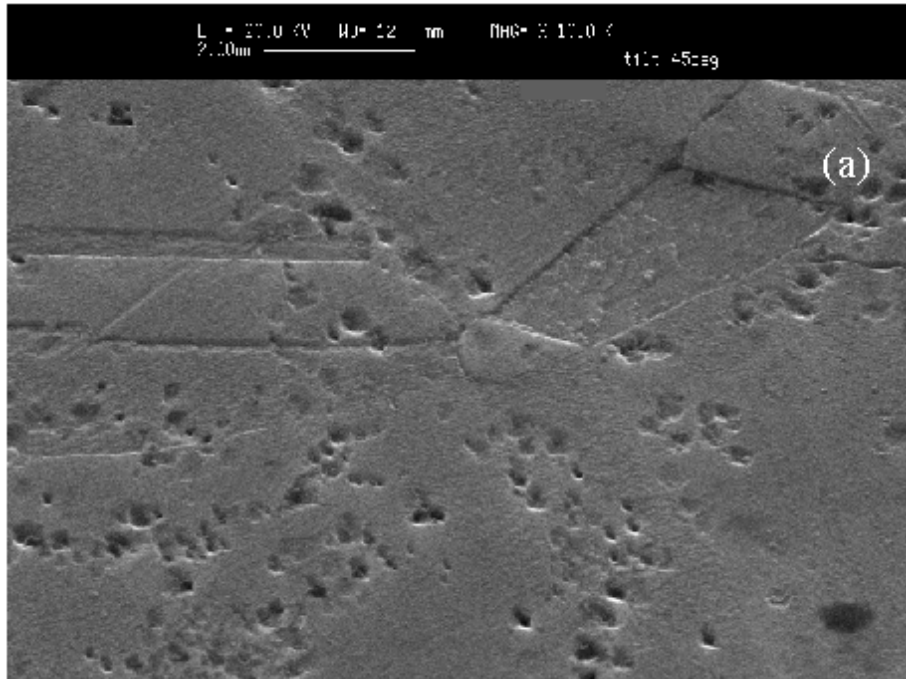
Figure 4 - Quality factors of cavities coated on electropolished copper substrates as a function of the accelerating gradient.
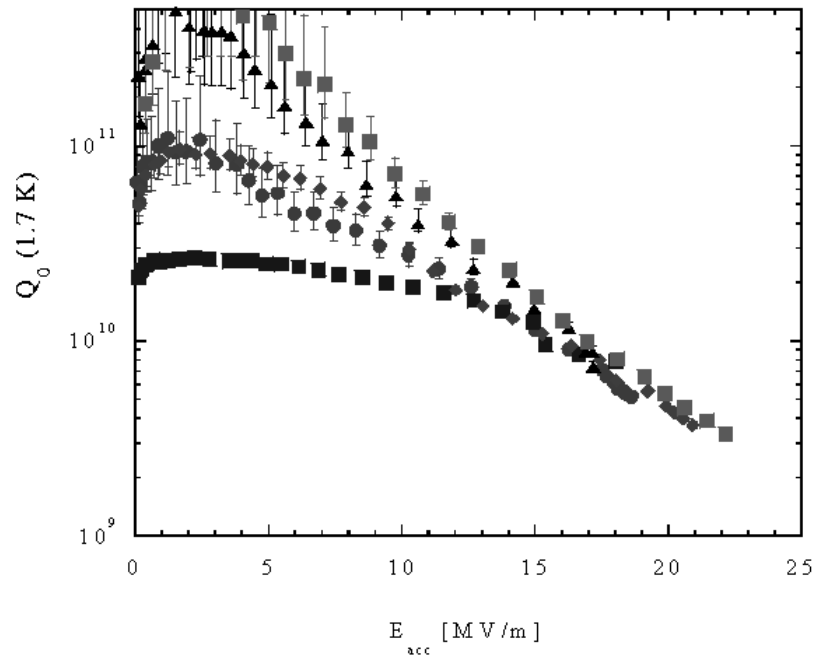
Figure 5 - Temperature dependence of the hydrogen partial pressure in the (closed) cavity volume for standard films (not loaded with hydrogen), (a) film grown on oxidised copper, (b) film grown on oxide-free copper. The lower branches correspond to the first heating cycle, the upper branches to the reversible equilibrium state reached thereafter.
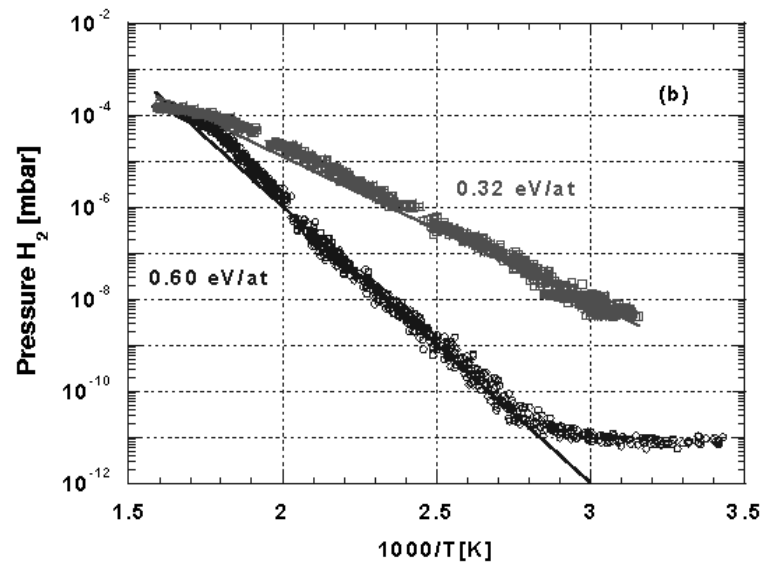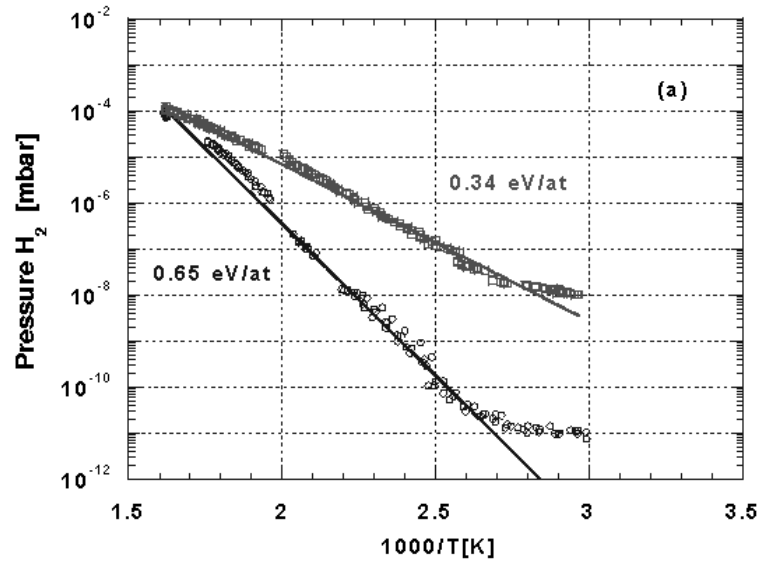
Figure 6 - Distribution of different films in the R_{res}^{1} vs R_{res}^{0} plane. The label indicates which noble gas was used for sputtering. Shown are films grown on hydroformed chemically polished copper (squares), on spun chemically polished copper (circles) and on spun electropolished copper (diamonds).